

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 10-297945

(43)Date of publication of application : 10.11.1998

(51)Int.Cl.

C03C 27/12
B32B 17/10

(21)Application number : 09-110958

(71)Applicant : CENTRAL GLASS CO LTD

(22)Date of filing : 28.04.1997

(72)Inventor : KONDO TAKESHI
YAMAMOTO HIDEKI**(54) SAFETY GLASS AND ITS PRODUCTION****(57)Abstract:**

PROBLEM TO BE SOLVED: To provide heat insulating performances, ultraviolet light screening performances, electric wave transmitting performances, etc., without influencing bond strength between glass and an intermediate film layer and to secure colored color tone, transparency, reflection prevention, etc., by laying a laminated intermediate layer of three layers between two sheets of plate glass-like materials and dispersing functional ultrafine particles having specific particle diameters or smaller than those on the second layer of the intermediate layer.

SOLUTION: Various metals, oxides, complexes, inorganic pigments, etc., are used as functional ultrafine particles dispersed on the second layer of an intermediate layer and the particle diameters of the particles are $\leq 0.2 \mu\text{m}$. Preferably the particle diameters are about 0.1–about $0.001 \mu\text{m}$ and the particle diameter distribution is uniformed. The first layer and the third layer are preferably a polyvinyl butyral film. The second intermediate film is a polyvinyl butyral resin or a vinyl chloride resin. The second intermediate film used is a raw material resin obtained by heating and softening a polyvinyl butyral resin at $55-90^{\circ}\text{C}$, mixing and kneading the resin with functional ultrafine particles in an amount of 10–0.01 wt.% to uniformly disperse the ultrafine particles.

LEGAL STATUS

[Date of request for examination]

02.06.1999

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

3301591

[Date of registration]

26.04.2002

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

*** NOTICES ***

JPO and NCIPi are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] The glass laminate characterized by particle size making the interlayer of the 2nd layer in these three layers come to distribute a functional ultrafine particle 0.2 micrometers or less in the glass laminate which prepared the doubling interlayer which consists of three layers between the transparence glass plate-like objects of at least two sheets.

[Claim 2] The glass laminate according to claim 1 with which said 1st layer and 3rd layer interlayer are characterized by being polyvinyl butyral resin.

[Claim 3] The glass laminate according to claim 1 or 2 with which said 2nd layer interlayer is characterized by being polyvinyl butyral resin or vinyl chloride resin.

[Claim 4] the particle size of said functional ultrafine particle -- 0.15 to 0.001 micrometer it is -- glass laminate according to claim 1 characterized by things.

[Claim 5] The glass laminate according to claim 1 or 4 with which the mixed rate of said functional ultrafine particle is characterized by being 10.0 - 0.01wt%.

[Claim 6] said functional ultrafine particle -- the metal of Sn, Ti, Si, Zn, Zr, Fe, aluminum, Cr, Co, In, nickel, Ag, Cu, Pt, Mn, Ta, W, V, and Mo, an oxide, a nitride, a sulfide or Sb, and F Glass laminate according to claim 1 characterized by being each independent object of a dope object, or the composite which comes to choose at least two or more sorts from these.

[Claim 7] The glass laminate according to claim 1 with which said glass laminate is characterized by being a windowpane for automobiles.

[Claim 8] The manufacture approach of the glass laminate characterized by making the interlayer of the 2nd layer in these three layers distribute a functional ultrafine particle 0.2 micrometers or less, and carrying out glass laminate-ized processing for the glass plate of at least two sheets in the approach of manufacturing the laminated glass which prepared the interlayer layer which consists of three layers between the transparence glass plate-like objects of at least two sheets.

[Claim 9] said interlayer film of the 2nd layer -- particle size 0.2 micrometers Make it distribute and it considers as a functional particle distribution plasticizer. the following functional ultrafine particles -- the inside of a plasticizer -- less than [80.0wt%] -- Subsequently, the manufacture approach of the glass laminate according to claim 8 characterized by being the resin film which consists this functional ultrafine particle distribution plasticizer of raw material resin distributed to homogeneity in a functional ultrafine particle to resin by 50wt (s)%, with carrying out the Shimowake powder addition and carrying out mixed kneading.

[Claim 10] Particle size to the solvent which dissolves polyvinyl butyral resin 0.2 micrometers Following 0.001 After distributing the functional ultrafine particle more than mum to homogeneity, [said interlayer of the 2nd layer] After making homogeneity dissolve this solvent in polyvinyl butyral resin with a plasticizer and other additives suitably and carrying out mixed kneading, The manufacture approach of the glass laminate according to claim 8 or 9 characterized by being the polyvinyl-butylal-resin film which film-ized from this raw material resin for interlayers, and was dried and obtained by 50 - 110 **.

[Claim 11] Said particle size at least said interlayer of the 2nd layer to the polyvinyl butyral resin which heated beyond the temperature of 55-90 degrees C which is a glass transition point, and was softened 0.2 micrometers Following 0.001 The manufacture approach of the glass laminate according to claim 8 characterized by being the polyvinyl-butylal-resin film which adds the functional ultrafine particle more than mum directly, carries out mixed kneading, and consists of raw material resin for interlayers which carried out homogeneity distribution.

[Translation done.]

*** NOTICES ***

JPO and NCIPI are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the glass laminate which has the engine performance excellent in an adhesive property, transparency, and endurance.

[0002]

[Description of the Prior Art] functional grant of the clearance in recent years and structural glass, coloring and heat insulation, ultraviolet-rays cutoff, electric-wave transparency, etc., etc. -- of course -- the glass for vehicles -- also setting -- in the car -- a connoisseur -- the solar-radiation energy which carries out ON is covered, and from the purpose which reduces a temperature rise in the car and a cooling load, further, human material both sides and in order to make it environment-friendly, heat ray electric shielding glass and the thing which added ultraviolet-rays electric shielding are adopted as vehicles. Moreover, in this glass for vehicles, the high permeability ability of various electric waves is especially required increasingly with the high temperature line ultraviolet-rays electric shielding engine performance recently, having sufficient light permeability in the Green color tone. Among those, the following applications are known as what distributes a particle or an ultrafine particle to the interlayer of laminated glass.

[0003] For example, the interlayer for short wave Nagamitsu line cutoff nature laminated glass which made plasticization polyvinyl butyral resin contain a light absorption agent and the particle-like unlimited matter is indicated by JP,2-22152,A, the glass laminate for automobiles which comes to form the mixolimnion of an ultrafine particle and a glass component between transparence plate-like part material is indicated by JP,4-160041,A, further, in JP,4-261842,A, it has the interlayer which contained the silicon-dioxide particle to ethylene ethyl acrylate copolymerization resin, and the glass laminate indication is carried out at it. Furthermore, the glass laminate which made the doubling interlayer distribute a functional particle is indicated by two glass laminates (Japanese Patent Application No. No. 007944 [07 to], No. 165489 [07 to]) of application of our company.

[0004] However, doubled the functional ultrafine particle, it was made to mix in an interlayer, bond strength with an interlayer was influenced together with glass with adhesion, the class of mixed particle which carries out laminating processing, the amount of mixing, particle diameter, etc. in direct glass and this interlayer, and the aforementioned glass laminate was not desirable. For example, when a particle was an oxide system, the bond strength with glass increased, when it was an object for automobiles, the impact absorptive power at the time of glass laminate destruction decreased, and there was a trouble on insurance.

[0005]

[Problem(s) to be Solved by the Invention] It is distributing in an interlayer layer suitably and making it contain a functional ultrafine particle, without affecting the interlayer layer for laminated glass which makes this invention in view of such a conventional technical problem, and is used from the former. Functional characteristics, such as heat insulation property, ultraviolet-rays cutoff engine performance, and electric-wave permeability ability, are given, moreover, it glares with reservation and reflexivity of control of the color tone of a clearance thru/or coloring, and fluoroscopy nature, and prevention of admiration etc. is brought about with sufficient balance. **, Can acquire the quality which is not different from conventional laminated glass, and neither special component presentation glass nor special surface treatment glass is needed. And it remains as it is and a laminated-glass production line present in use can be performed by the laminated-glass-ized processing activity. For example, cheaply, easy moreover, it can respond to the magnitude and the gestalt of glass freely,

and glass, glass and glass, plastics, bilayer glass, etc. can be manufactured. Of course, structural aperture material offers the aperture material for automobiles, the aperture material for airplanes, and the useful functional laminated glass that can apply also to the glass for windshields enough especially, and becomes the optimal thing for the latest needs.

[0006]

[Means for Solving the Problem] This invention offers the laminated glass characterized by particle size making the interlayer of the 2nd layer in these three layers come to distribute a functional ultrafine particle 0.2 micrometers or less in the laminated glass which prepared the doubling interlayer which consists of three layers between the transparency glass plate-like objects of at least two sheets.

[0007] Said 1st layer and 3rd layer interlayer are polyvinyl-butylal-resin film preferably.

[0008] Said 2nd layer interlayer is polyvinyl butylal resin or vinyl chloride resin preferably.

[0009] the particle size of said functional ultrafine particle -- more -- desirable -- 0.15 to 0.001 micrometer it is .

[0010] The mixed percentage of said functional ultrafine particle is 10.0 - 0.01wt% preferably.

[0011] Said functional ultrafine particle Sn, Ti, Si, Zn, Zr, Fe, aluminum, Cr, Co, In, nickel, Ag, Cu, Pt, Mn, Ta, W, and V, A metal, an oxide, a nitride, a sulfide, or Sb and F of Mo It is the coat object which covered each independent object of a dope object, the composite which comes to choose at least two or more sorts from these, the mixture which contains an organic resin object in each independent object or a composite concerned further, or an organic resin object.

[0012] Said glass laminate is suitable as a windowpane for automobiles.

[0013] Moreover, in the approach of manufacturing the laminated glass which prepared the interlayer layer which consists of three layers between the transparency glass plate-like objects of at least two sheets, this invention makes the interlayer of the 2nd layer in these three layers distribute a functional ultrafine particle, and offers the manufacture approach of the laminated glass characterized by carrying out glass laminate-ized processing for the glass plate of at least two sheets.

[0014] moreover, this invention -- said interlayer of the 2nd layer -- particle size 0.2 micrometers Make it distribute and it considers as a functional ultrafine particle distribution plasticizer. the following functional ultrafine particles -- the inside of a plasticizer -- less than [80.0wt%] -- Subsequently, the manufacture approach of the laminated glass characterized by being the resin film which consists this functional ultrafine particle distribution plasticizer of raw material resin distributed to homogeneity in a functional particle to resin by 50wt(s)%, with carrying out the Shimowake powder addition, adding other additives suitably, and carrying out mixed kneading is offered.

[0015] Furthermore, said particle size this invention to the solvent which dissolves polyvinyl butylal resin 0.2 micrometers Following 0.001 After distributing the functional ultrafine particle more than mum to homogeneity, [said interlayer of the 2nd layer] Suitably, with a plasticizer and other additives, make polyvinyl-butylal system resin carry out the homogeneity dissolution, carry out mixed kneading, and the solvent concerned is film-ized from the raw material resin for film. The manufacture approach of the laminated glass characterized by being the polyvinyl-butylal system resin film dried and obtained by 50 - 110 ** is offered.

[0016] As for this invention, said particle size at least said interlayer of the 2nd layer further again to the polyvinyl butylal resin which heated beyond the temperature of 55-90 degrees C which is a glass transition point, and was softened 0.2 micrometers Following 0.001 The manufacture approach of the laminated glass characterize by be the polyvinyl butylal system resin film which added the functional ultrafine particle more than mum directly, and carried out mixed kneading, and which was obtained from the raw material resin for film which carried out homogeneity distribution is offer.

[0017]

[Embodiment of the Invention] Here, as described above, particle size is 0.2 in the 2nd interlayer layer. mum Making it come to distribute the following functional ultrafine particles Solar radiation permeability demonstrating enough the functional characteristic of particles, such as heat ray electric shielding engine performance, such as 65 etc.% or less, for example controlling the scatter reflection of a light region In order to secure a super-low haze value, electric-wave permeability ability, and transparency, it is because physical properties, such as an adhesive property, transparency, and endurance, are maintained as a conventional interlayer for laminated glass even if it makes an ultrafine particle contain, and it can usually be made to

perform laminated-glass-ized processing in an activity with the usual laminated-glass production line. Particle size is 0.15 micrometers preferably. It is [following] extent and is about 0.10-0.001 more preferably. It is extent. In addition, about the range of particle size distribution, it is about 0.03-0.01 micrometers, for example. It is good to be equalized with extent.

[0018] Moreover, having presupposed that the mixed rate of the functional ultrafine particle to the 2nd interlayer layer is less than [10.0wt%] The amount in which solar radiation permeability demonstrates enough the functional characteristic of ultrafine particles, such as heat ray electric shielding engine performance, such as 65 etc.% or less, for example is secured controlling the scatter reflection of a light region. Even if it makes it be a low haze value, electric-wave permeability ability, and transparency furthermore and moreover makes an ultrafine particle contain, as a conventional interlayer for laminated glass For example, an adhesive property, Physical properties, such as transparency and endurance, are maintained and it is because [according to / the usual laminated-glass production line] it can usually be made to perform laminated-glass-ized processing in an activity. When said particle size has a close relation and comes to exceed 10.0wt%, it is because especially the aperture material for automobiles, of course, stops being able to realize the above-mentioned requirements easily also as structural aperture material gradually. When the light permeability Tv is 35% or more as for structural laminated glass especially, for example, the mixed rate of an inorganic pigment system ultrafine particle is the about [abbreviation 10-0.1 wt%] need. It is about 8-0.05wt% more preferably. as the object for construction -- about 9 -- about -0.01wt% -- mixing desirable as an object for automobiles -- if it carries out comparatively -- about 2.0 -- about -0.01wt% -- more -- desirable -- about 1.5 -0.05wt% -- it is 1.0 - 0.1wt % extent still more preferably. Anyway, the mixed rate (content) is determined on the balance of the engine-performance maintenance as laminated glass, and the functional ability to aim at.

[0019] Furthermore, since these are the things of versatility as an interlayer for laminated glass, it is desirable that the interlayer carried out the polyvinyl-butylal system resin film (PVB system), and especially if it becomes the interlayer layer which can adjust the quality as laminated glass for needs, it will not limit. In a concrete target, it is plasticity PVB. The addition combination of [the Sekisui Chemical Co., Ltd. make, the Mitsubishi Monsanto Co. make, etc. ultraviolet ray absorbents], an anti-oxidant, an antistatic agent, a thermostabilizer, lubricant, a bulking agent, coloring, the adhesion regulator, etc. can be carried out suitably. moreover, the thing for which the sound isolation engine performance is improved when vinyl chloride resin is used as the 2nd interlayer -- things are made and it is desirable.

[0020] Moreover, ethylene-vinylacetate copolymer resin can also be used as an interlayer, it is desirable that the 2nd interlayer also uses the same resin in that case, and it is suitable for especially a structural glass laminate.

[0021] In addition, both are piled up for this interlayer containing an ultrafine particle, and the conventional interlayer as an interlayer. Or it is good also as what is considered as the configuration of sandwiching this interlayer containing an ultrafine particle by the conventional interlayer.

[0022] A functional ultrafine particle Furthermore, Sn, Ti, Si, Zn, Zr, Fe, aluminum, Cr, Co, Ce, In, nickel, Ag, Cu, Pt, Mn, Ta, The metal of W, V, and Mo, an oxide, a nitride, a sulfide, or Sb and F Each independent object of a dope object, Or the composite which comes to choose at least two or more sorts from these, That or it shall be the coat object which covered the mixture or the organic resin object which contains organic resin in an independent object or a composite concerned further It is for discovering suitably heat insulation property, the ultraviolet-rays electric shielding engine performance, the coloring engine performance, protection-from-light nature, etc. as each independent one or a composite, mixture, and a coat object, and making various functionality and engine performance for which the object for construction and automobiles are asked discover as laminated glass.

[0023] moreover -- as a functional ultrafine particle -- Sn, Ti, Si, Zn, Zr, Fe, aluminum, Cr, Co, Ce, In, nickel, Ag, Cu, Pt, Mn, Ta, W, and V etc. -- others -- various metals, such as Mo. for example, SnO₂, TiO₂, SiO₂, ZrO₂, ZnO, and Fe₂O₃ aluminum₂O₃ FeO and Cr₂O₃ Co₂O₃ CeO₂ and In₂O₃ NiO, MnO, and CuO etc. -- various oxides. for example, TiN and AlN etc. -- a nitride or nitrogen oxides. for example, ZnS etc. -- sulfide. For example, 9wt%Sb₂O₃-SnO₂ (ATO) The [Sumitomo Osaka Cement make], dope object of F-SnO₂ grade. Further for example, they are SnO₂-10wt%Sb₂O₃ and In₂O₃-5wt%SnO₂ (ITO). They are composites, such as the [MITSUBISHI MATERIALS CORP. make]. In addition, ATO and ITO It has the requirement as an object for automobiles, and is especially desirable.

[0024] Further, for example Co₂O₃-aluminum₂O₃ (TM [3410], 0.01-0.02 micrometers), TiO₂-NiO-Co₂O₃-

ZnO (TM3320, 0.01-0.02 micrometers), Inorganic pigment particles, such as by Dainichiseika Colour & Chemicals Mfg. Co., Ltd., are mentioned, respectively. Fe₂O₃-ZnO-Cr₂O₃ (TM [3210], 0.01-0.02 micrometers) -- [-- Moreover, for example as TiO₂ ultrafine particle, it is specifically. IT-S-UD [0.02micrometer,] by the Idemitsu petrochemical company, and UF 01[0.018 mum, Tie Oxide Chemicals], etc., Fe₂O₃ As a particle, nano tightness [particle globular form hematite, 0.06 micrometers It cannot be overemphasized that it can be used without limiting especially if the functional characteristic suitably asked also for the particle which] by Showa Denko K.K. etc. is mentioned and is not mentioned concretely if needed can be demonstrated maintaining the quality of laminated glass.

[0025] furthermore, about an organic system ultraviolet ray absorbent or an organic system heat ray absorbent As an organic system ultraviolet ray absorbent, it is 2 - (2'- hydroxy-5'-methylphenyl) Benzotriazol, 2 - (2'-hydroxy [- Buthylphenyl] - 3', 5' - II and tert) Benzotriazol, 2-(2'-hydroxy-3'-tert-butyl -5'-methylphenyl)-5 - Chlorobenzo triazole, 2-(2'-hydroxy [- Buthylphenyl] - 3', 5' - II and tert)-5-chlorobenzo triazole, 2 - (2'-hydroxy [- Amyl phenyl] - 3', 5' - II and tert) Benzotriazol system derivatives, such as benzotriazol, Moreover, 2, 4-dihydroxy benzophenone, 2-hydroxy - 4 - Methoxybenzophenone, 2-hydroxy - 4 - Octoxybenzophenone, 2-hydroxy - 4 - Dodecyloxy benzophenone, 2 2' - Dihydroxy -4 - Methoxybenzophenone, 2, 2' - Dihydroxy -4, a 4'-dimethoxy benzophenone, 2-hydroxy - 4 - Methoxy -5 - Benzophenone system derivatives, such as a sulfo benzophenone, Moreover, 2-ethylhexyl - 2 - Cyano [- Cyanoacrylate system derivatives, such as 3 and 3'-diphenyl acrylate, etc. are mentioned.] - 3, 3'-diphenyl acrylate, ethyl -2 - Cyano Specifically, it is TINUVIN327 [the Ciba-Geigy make] etc.

[0026] Furthermore as an organic system heat ray absorbent, it is NIR-AM1. As a near infrared ray absorbent, it is SIR-114, SIR-128, SIR-130, SIR-132, SIR-169, SIR-103, PA-1001, and PA-1005 to [imperial chemistry industrial company make] and a thing. The [Mitsui Toatsu Chemicals, Inc. make] etc. is mentioned. Especially the thing that can be used without limiting if it demonstrates maintaining the quality of the laminated glass for which the object for construction and automobiles are asked cannot be overemphasized.

[0027] furthermore, the thing for which the laminated glass which becomes with said configuration carried out can be used as various structural aperture material etc. -- of course -- especially -- as the aperture material for automobiles -- for example, a windshield and rear glass -- it can be used for rear glass with a shade band, side glass, sunroof glass, or other various glass at things.

[0028] Generally moreover, as sheet resistance of glass with a glass antenna for example, in case it is the resistance more than 20Kohm/opening and especially an antenna is contacted It is desirable that it is the high resistance 10M omega / more than opening. In the sheet resistance of under 10M omega / opening It is what cannot compare with the electric-wave permeability of the glass plate before making it a layered product, and cannot be stored in the fluctuation difference within 1dB sufficiently stably certainly (as an absolute value). In order [sufficiently stable] to consider as the inside of the fluctuation difference within a less than 1dB fluctuation difference (for example, less than 0.8 dB) certainly, more than 15M omega / opening As sheet resistance of the desirable layered product which furthermore satisfies enough electric-wave permeability ability, an optical property, and physical chemical property, it is the range of 10G omega / below opening extent more than 20M omega / opening. As more desirable sheet resistance, it is the range of 10G omega / below opening extent more than 22M omega / opening.

[0029] this glass plate-like object and said layered product which has almost equivalent electric-wave permeability ability -- especially -- an optical property top -- skillful -- mutual -- twining -- the synergistic effect -- bringing -- **** -- it considers as what [equipped with the optical function which was markedly alike and was excellent in making it like as well as having raised electric-wave permeability ability and the heat ray electric shielding engine performance] that stood high and is the optimal as a windowpane for automobiles especially.

[0030] that is, electric-wave permeability ability being brought close to said glass plate-like object infinite, and it supposing that it is almost equivalent as a windowpane for automobiles, and solar radiation permeability looking like [65% or less] the heat ray electric shielding engine performance markedly, raising it, and amenity in having improved further The fluoroscopy nature which made the light permeability which an operator, a passenger, etc. need in insurance superiors 65% or more, For example, light permeability secures 70 etc.% or more etc., and can make it possible to also clear a regulation top. And a light reflection factor required for prevention of the fluoroscopy nature fall in an operator, a passenger, etc., misconception, or fatigue of an eye

can be made to reduce further from the conventional value, and it becomes the optimal electric-wave transparency mold heat ray ultraviolet-rays electric shielding laminated glass. For 68 - 70% or more, and a light reflection factor, moreover, solar radiation permeability is [light permeability / 60% or less and excitation purity] 15 - 10% or less 14% or less preferably as an object for automobiles, and, for 30% or more and a light reflection factor, moreover, solar radiation permeability is [light permeability / 65% or less and excitation purity] 20% or less 20% or less preferably as an object for construction.

[0031] Further again the laminated glass of said electric-wave transparency mold heat ray ultraviolet-rays electric shielding For example, a perimeter part or a little larger part than the feeding point section is removed from a periphery edge by a certain width of face within the black frame of the periphery of a glass plate-like object. or the part which moreover really casts or post-installs a mall (frame) like this feeding point section -- removing -- further -- this antenna -- a conductor -- it cannot be overemphasized that the configuration, such as adopting the functional interlayer which contains an ultrafine particle except for all or a part of parts, can be made free suitably.

[0032] An interlayer has the heat ray electric shielding engine performance, and the glass which can be prevented from discovering more certainly electromagnetic interferences, such as a ghost phenomenon in the radio disturbance or TV image in broadcast of AM electric wave, FM electric wave, etc., etc. by being the semiconductor film thru/or an insulator layer, and a high value about sheet resistance, and has sufficient electric-wave permeability ability can be obtained further again, and it can consider as an environment-friendly thing. Moreover, when the direct laminating of the film which has said heat ray electric shielding engine performance of high resistance is carried out to a glass antenna element for example, it can be said that it was made not to affect electric-wave receiving performance degradation.

[0033] Moreover, glass, the primer, the various functional film, etc. which is similar to a transparent clearance thru/or colored glass, tempered glass, or it as a glass plate-like object as mentioned above with minerals glass, organic glass or these compound glass, and the minerals manufactured especially with the so-called float glass process are glass with the covering film, is Green system glass and bronze system glass preferably, and can be adopted as gray system glass, blue system glass, etc. further, for example. Moreover, things which can be further used as various sheet glass products, such as a plate or a bending plate, such as multiple glass besides laminated glass and bilayer glass, cannot be overemphasized. Moreover, as board thickness, it is about 1.0mm. It is about 12mm or less more than extent, and is about 2.0mm as an object for construction. About 10mm or less is desirable more than extent, and it is about 1.5mm as an object for automobiles. It is about 3.0mm more than extent. Below extent is desirable and it is about 2.0mm more preferably. It is about 2.5mm more than extent. It is glass below extent.

[0034] Furthermore, the polyvinyl-butyral-resin film or the ethylene-vinylacetate copolymer resin film particle size -- 0.2 μ m Make it distribute and it considers as a functional ultrafine particle distribution plasticizer. the following functional ultrafine particles -- the inside of a plasticizer -- less than [80.0wt%] -- This functional ultrafine particle distribution plasticizer subsequently, in a polyvinyl-butyral system or an ethylene-vinylacetate copolymer resin solution Distributed addition is carried out at least. a polyvinyl-butyral system or ethylene-vinylacetate copolymer resin -- receiving -- a functional ultrafine particle distribution plasticizer -- less than [50wt%] -- That we decided to have added other additives suitably, to have carried out mixed kneading, and to have obtained from the raw material resin for film It is easy to distribute the direction which makes said functional ultrafine particle distribute in a plasticizer solution. Particle size is 0.2. Distribution of the functional ultrafine particle below μ m can be equalized enough. It is because transparency is acquired and is because distribution will become difficult and equalization will become becoming is easy to be trustworthy less gradually, if the amount of mixing exceeds 80.0wt(s)%. desirable -- or less about 20.0wt% -- more -- desirable - - or less about 10.0wt% -- still more preferably, it is extent more than below 5.0wt(s) %0.5wt %, and even if too few, said effectiveness is lost.

[0035] moreover -- if distributed addition of a functional ultrafine particle distribution plasticizer exceeds 50wt (s)% to a polyvinyl butyral or ethylene-vinylacetate copolymer resin, since it will be easy to come to cause trouble to the engine performance as an interlayer of not only distribution in a polyvinyl butyral or ethylene-vinylacetate copolymer resin but laminated glass -- it is -- desirable -- or less about 45wt% -- it is beyond about or less about [40wt%] 10wt% more preferably. Moreover, the usual mixer, a Banbury mixer and the Brabender mixer, a kneader, etc. are used for mixed kneading.

[0036] As a plasticizer, further again, for example Dioctyl phthalate (DOP), Di-isodecyl phthalate (DIDP), di-tridecyl phthalate (DTDP), butyl benzyl phthalate (BBP) etc. -- phthalic ester and tricresyl phosphate (TCP) -- trioctylphosphate (TOP) etc. -- phosphoric ester and tributyl citrate -- methyl acetyl triricinolate (MAR) etc. -- fatty-acid-ester and triethylene glycol G 2- Such mixture, such as polyether ester, such as ethyl butyrate (3GH) and tetraethylene glycol dihexanol, is mentioned.

[0037] Furthermore, said PVB As a solvent which dissolves system resin, ethyl alcohol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, a methylene chloride, etc. are mentioned, for example. It is said EVA further again. As a solvent which dissolves system resin, toluene, a xylene, a methylene chloride, etc. are mentioned, for example.

[0038] Furthermore, as film-izing of said raw material resin for interlayers, it is a mold extrusion method or the calendering roll method of a conventional method etc. as the thickness of an interlayer -- about 0.2-1.2mm extent -- desirable -- about 0.3-0.9mm It is extent.

[0039] Furthermore, as said laminated-glass-ized processing, while carrying out a temperature up from ordinary temperature to 120 ** under the autoclave method and reduced pressure, it is heating for 20 - 30 minutes etc. in the temperature requirement of 80 - 120 **, and the crimp of uniform irregularity is prepared in a film front face. In addition, it cannot be overemphasized that various simple laminated-glass-ized processings are applicable suitably with a case.

[0040]

[Function] The laminated glass of this invention as mentioned above Coloring, a heat ray and ultraviolet-rays cutoff film, By having carried out distributed content of the ultrafine particle which has various kinds of functional ability, such as electric-wave transparency, suitably into the interlayer of the 2nd layer, and having considered as the laminated glass which becomes by doubling and processing, and its manufacture approach Without affecting the interlayer layer for laminated glass currently used from the former Functional characteristics, such as heat insulation property, ultraviolet-rays cutoff engine performance, and electric-wave permeability ability, are given, moreover, control and the haze value of the color tone of a clearance thru/or coloring glare with reservation and reflexivity of the fluoroscopy nature excellent very low, and prevention of admiration etc. is brought about with sufficient balance. **, For example, each trial of JIS R 3212 concerning the safety glass for automobiles etc. is cleared, Can acquire the quality which is not different from conventional laminated glass, and neither special component presentation glass nor special surface treatment glass is needed. And it remains as it is, a laminated-glass production line present in use can be performed by laminated-glass-ized processing and the activity, easy moreover, it can respond to the magnitude and the gestalt of glass freely cheaply, and laminated glass can be obtained. Moreover, fluoroscopy nature, weatherability, shock resistance, etc. are excellent in the laminated glass using the bipolar membrane which carried out the adhesion laminating of the vinyl chloride system resin film becoming what is excellent in penetration-proof, soundproofing, etc. in addition to the property mentioned above, and turning into a windowpane for automobiles useful as front window shield glass etc., and the windowpane for automobiles which can be contributed to crew's safety in the car, amenity, etc. is offered.

[0041] As a result, while having the ultraviolet-rays cutoff which becomes kind to solar radiation permeability, a great environment, and a great man who the air conditioning effectiveness is heightened [man] and make amenity improve It shall have visible-ray permeability broad from a comparatively high thing to a low thing. Radio disturbance in broadcast of AM electric wave, an FM electric-wave TV electric-wave band, etc. can be reduced. Television for vehicles since it is the electric-wave transparency engine performance of the usual float glass average, Without reducing the receiving engine performance of the glass antenna for radio, a cellular phone, etc. Or can reduce electromagnetic interferences, such as a ghost phenomenon, and the original glass antenna engine performance is demonstrated. Colored [colorlessness to] and the various color tones which can secure vehicle inside and outside and a comfortable environment, and need electric-wave permeability ability, Or it becomes electric-wave transparency mold heat ray ultraviolet-rays electric shielding glass usable as glass, glass and glass, and laminated glass, such as a synthetic-resin plate and a bilayer, etc. The aperture material for automobiles, for example, a front window, of course especially as structural aperture material In a rear window, a side window or a sunroof, a shade band, etc. It can apply also to the glass for windshields enough especially, and the aperture material for airplanes etc. can be applied broadly, and the laminated glass which has the useful functionality used as the optimal thing for the latest needs, and its manufacture approach are offered.

[0042]

[Example] Hereafter, an example explains this invention concretely. However, this invention is not limited to the starting example.

[0043] Example 120wt%ATO (conductive antimony content stannic acid ghost) Ultrafine particle (particle size of 0.02 micrometers following) distribution content DOP (dioctyl phthalate) 10 g and usual It is PVC (polyvinyl chloride) about DOP 100g. Resin It added to 450g, and with other ultraviolet ray absorbents etc., it grade-scoured for about 15 minutes at about 70 degrees C by the mixer of 3 rolls, and mixed. It is the thickness of about 0.8mm before and after 190 ** with a die pressing appearance machine about the obtained raw material resin for film production. It film-ized to extent and rolled round on the roll. Let this be a film (A).

[0044] Next, the film (B) of two sheets and film (A) which were obtained from polyvinyl butyral resin were piled up so that a laminating configuration might become the polyvinyl-butyr-al-resin (layer B) / polyvinyl chloride resin (layer A) / polyvinyl-butyr-al-resin layer (B), and the laminating interlayer of three layers was obtained. After having sandwiched this interlayer from both sides with the float glass with a thickness [2.3mm] of with an one-side square [30cm square] of two sheets, respectively, putting this non-stuck by pressure sandwiches object into the rubber back and carrying out indirect desulfurization mind with the degree of vacuum of 20torr for 20 minutes, it moved to 90-degree C oven with the degassing condition, and this temperature was held for 30 minutes. In this way, subsequently to the inside of an autoclave, thermocompression bonding processing of the sandwiches object which carried out temporary sticking by pressure with the vacuum press was carried out at pressure 2 and temperature of 135 degrees C of 12kg/cm, and the transparent glass laminate was produced.

[0045] Subsequently, degassing reduced pressure of the inside of a bag is carried out, this layered product is put into the vacuum bag made of rubber, after holding about about 20 to 30 minutes with about 80 - 110 ** extent, it once carries out by ordinary temperature, and the layered product taken out from the bag is put into autoclave equipment, and it is the pressure of about 10-14kg/cm². The grade carried out pressurization heating for about 20 - 40 minutes with temperature 110 [about] - 140 ** extent, and laminated-glass-ized processing was carried out.

[0046] Following measurement and evaluation were performed about the obtained laminated glass.

[Optical property]: The permeability of a between with a wavelength of 340-1800nm was measured with the spectrophotometer (340 the account of type **, Hitachi make), and the light permeability Tv (380-780nm), the solar radiation permeability Ts (340-1800nm), excitation purity, a color tone, etc. were searched for(%) by JIS Z8722 and JIS R3106, or JIS Z 8701.

[Whenever [cloudy]]: Haze value H JIS K6714 It was based and asked by carrying out. As an object for construction, 1% or less was considered as success as an object for automobiles 3% or less.

[Electric-wave permeability] :KEC By method measurement (electric-field shielding-effect measuring instrument), it is 3mm of the usual board thickness about the reflection loss value (dB) of the range of 10-1000MHz of electric waves. A clear glass (floor line3t) veneer article and contrast. The absolute value (**dB) of the difference considered less than 2dB as success.

[Adhesive property]: It is 16**4 at the temperature of -18**0.6 **. Time amount neglect is carried out and it is interlayer exposure extent in exfoliation of the glass after adjustment and in hammer **. Few things were considered as success.

[Thermal resistance]: It is 2 at the boiling underwater of 100 **. After carrying out time amount extent boiling, except for 10mm of circumferences, the thing without abnormalities, such as a crack of generating of ** in the remaining part, cloudy weather, and glass, was considered as success.

[Moisture resistance]: After putting for two weeks into adjustment of 50**2 ** and relative humidity 95**4 %, the thing without abnormalities, such as a crack of generating of **, cloudy weather, and glass, was considered as success.

[Electrical characteristics]: Measure with the Mitsubishi Petrochemical tabulation side quantity ohm-meter (HIRESTA HT-210). It passes more than 10M omega / opening (sheet resistance).

[0047] The solar radiation permeability Ts about 77.7% About 55.0%, [a result and the light permeability Tv] The neutral color tone of a gray system with excitation purity Pe light at 0.7 % extent, There is also no flash by reflection and the haze value H serves as abbreviation 0.3 % extent. optical properties, such as excellent enough heat ray electric shielding nature, -- markedly -- alike -- high surface resistivity -- usually -- the veneer glass

average -- for example, 80MHz (FM radio band) About 520-1630kHz (AM radio band) Electric-wave permeability equivalent to veneer glass is usually shown especially. etc. -- And sufficiently stable adhesive property, outstanding thermal resistance, and outstanding moisture resistance are shown, and all are success. The laminated glass which is not different from usual laminated glass can be obtained, with the outstanding amenity, it is kind to an operator, a passenger, or an environment, safety is high, moreover, AM band is begun, and reception can do various electric waves comfortably. a structural windowpane is natural -- the windowpane for automobiles -- especially -- an antenna -- it was what can adopt enough also to a conductor, simultaneously the windowpane for automobiles which it has, and can reply to expectation enough.

[0048] In addition, when various properties, such as weatherability (change should not have about 1000 hour:light permeability mostly at an example and a sunshine weather meter), were otherwise evaluated, it was what all pass.

[0049] Furthermore, in the windowpane for automobiles of the same configuration, when controlled to hold said interlayer to a 10 degrees C - 50 degrees C temperature requirement, it was what obtains the same result with having mentioned above and contributes to the silence of the vehicle interior of a room enough.

[0050] in addition, the obtained sample -- the gaging system of acoustic radiation power -- acoustic radiation power -- measuring -- a reverberation method -- sound transmission loss -- measuring -- further -- JIS 3211, JIS 3212, and JIS R3205 etc. -- when evaluated according to the convention, it had enough the engine performance as an expected windowpane for automobiles, and excelled.

[0051] example 220wt%ATO (conductive antimony content stannic acid ghost) Ultrafine particle (particle size of 0.02 micrometers following) distribution content 3GH (triethylene glycol-G 2- ethyl butyrate) It is PVB (polyvinyl butyral) about 10 g and the usual 3GH 130 g. Resin It adds to 485g. Furthermore, it is TOSUPA-RU 120 (Toshiba Silicone) as an adhesion regulator. 5g added, and with other ultraviolet ray absorbents etc., it grade-scoured for about 15 minutes at about 70 degrees C by the mixer of 3 rolls, and mixed. It is the thickness of about 0.8mm before and after 190 ** with a die pressing appearance machine about the obtained raw material resin for film production. It film-ized to extent, rolled round on the roll, it sandwiched with the polyvinyl-butyr-al-resin film like the example 1, and the three-layer layered product was obtained.

[0052] Next, about 2.0mm in magnitude abbreviation 300mmx300mm and thickness Clear glass substrate (floor line2) It used and doubled like the example 1. Subsequently, laminated-glass-ized processing was carried out like the example 1.

[0053] The obtained laminated glass was an expected thing which shows each physical properties, such as an optical property Tv was excellent 80.2% and Ts was excellent in H of an optical property like the examples 1, such as 0.4 %, 58.5% and electric-wave permeability, and quality, with sufficient balance.

[0054] Example 320wt%ITO (conductive tin content indium oxide) Ultrafine particle (particle-size 0.1 mum following) distribution content BBP (butyl benzyl phthalate) 10 g and usual It is PVC resin about BBP70g. It added to 300g and glass laminate-ized processing was carried out like the example 1.

[0055] Next, about 2.0mm in magnitude abbreviation 300mmx300mm and thickness Clear glass substrate (floor line2) It used and considered as the layered product like the example 1. Subsequently, laminated-glass-ized processing was carried out like the example 1.

[0056] The obtained laminated glass was an expected thing which shows each physical properties, such as an optical property Tv was excellent 71.3% and Ts was excellent in H of an optical property like the examples 1, such as 0.4 %, 46.1% and electric-wave permeability, and quality, with sufficient balance. Moreover, the pan mel value was seven to about eight, and was a thing suitable for structural laminated glass.

[0057] In addition, it cannot be overemphasized that it carries out like an example 3 also in examples 1 and 2, and it can adjust as the object for construction or an object for automobiles suitably, and can use about a pan mel value.

[0058]

[Effect of the Invention] As mentioned above, this invention by having made the functional ultrafine particle into the laminated glass which carries out distributed content, and its manufacture approach at the interlayer layer Without having big effect on the interlayer layer for laminated glass currently used from the former Functional characteristics, such as heat insulation property, ultraviolet-rays cutoff engine performance, and electric-wave permeability ability, are given, moreover, control and the haze value of the color tone of a clearance thru/or coloring glare with reservation and reflexivity of the fluoroscopy nature excellent very low,

and prevention of admiration etc. is brought about with sufficient balance. **, The quality which is not different from conventional laminated glass can be acquired, it remains as it is and a laminated-glass production line present in use can be performed by laminated-glass-ized processing and the activity. Cheaply, easy moreover, it can respond to the magnitude and the gestalt of glass freely, and can carry out. As a result, heighten the air conditioning effectiveness, make amenity improve, and are kind to an environment or a man. Broad fluoroscopy nature can be obtained. AM electric wave, an FM electric-wave TV electric-wave band, etc. Television for [as electric-wave transparency engine performance of the usual float glass average] vehicles, Can secure the glass antenna engine performance for radio, a cellular phone, etc., and the original glass antenna engine performance is demonstrated. A building, and vehicle inside and outside and a comfortable environment can be secured. It becomes electric-wave transparency mold heat ray ultraviolet-rays electric shielding glass usable as laminated glass of colored and various color tones etc. from colorlessness. Of course especially as various structural aperture material, the various aperture material for automobiles, the laminated glass which has the useful functionality which can apply broadly the glass for windshields and the aperture material for airplanes, other industrial glass, etc. especially, and becomes the optimal thing for the latest needs, and its manufacture approach can be offered. Moreover, as mentioned above, according to the windowpane for automobiles of this invention, a loss factor is secured near maximum. Can make the whole glass into the high vibration-deadening-engine performance, and it excels in each property, such as sound, vibration, and noise insulation. The noise in the car which it is filled with the vehicle interior of a room, and contains a sound is reduced, silence is acquired, and the windowpane for automobiles which has Takayasu all nature and high amenity more is offered, such as becoming what is moreover excellent in fluoroscopy nature, weatherability and shock resistance, or penetration-proof.

[Translation done.]

PATENT ABSTRACTS OF JAPAN

(11)Publication number : **10-297945**

(43)Date of publication of application : **10.11.1998**

(51)Int.Cl.

C03C 27/12

B32B 17/10

(21)Application number : **09-110958**

(71)Applicant : **CENTRAL GLASS CO LTD**

(22)Date of filing : **28.04.1997**

(72)Inventor : **KONDO TAKESHI
YAMAMOTO HIDEKI**

(54) SAFETY GLASS AND ITS PRODUCTION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide heat insulating performances, ultraviolet light screening performances, electric wave transmitting performances, etc., without influencing bond strength between glass and an intermediate film layer and to secure colored color tone, transparency, reflection prevention, etc., by laying a laminated intermediate layer of three layers between two sheets of plate glass-like materials and dispersing functional ultrafine particles having specific particle diameters or smaller than those on the second layer of the intermediate layer.

SOLUTION: Various metals, oxides, complexes, inorganic pigments, etc., are used as functional ultrafine particles dispersed on the second layer of an intermediate layer and the particle diameters of the particles are $\leq 0.2 \mu\text{m}$. Preferably the particle diameters are about $0.1\text{--}0.001 \mu\text{m}$ and the particle diameter distribution is uniformed. The first layer and the third layer are preferably a polyvinyl butyral film. The second intermediate film is a polyvinyl butyral resin or a vinyl chloride resin. The second intermediate film used is a raw material resin obtained by heating and softening a polyvinyl butyral resin at $55\text{--}90^\circ \text{C}$, mixing and kneading the resin with functional ultrafine particles in an amount of $10\text{--}0.01 \text{ wt.}\%$ to uniformly disperse the ultrafine particles.

LEGAL STATUS

[Date of request for examination] 02.06.1999

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number] 3301591

[Date of registration] 26.04.2002

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

Copyright (C); 1998,2003 Japan Patent Office

(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開平10-297945

(43) 公開日 平成10年(1998)11月10日

(51) Int.Cl.⁸

識別記号

F I

C 0 3 C 27/12

C 0 3 C 27/12

K

B 3 2 B 17/10

B 3 2 B 17/10

審査請求 未請求 請求項の数11 O L (全 8 頁)

(21) 出願番号 特願平9-110958

(22) 出願日 平成9年(1997)4月28日

(71) 出願人 000002200

セントラル硝子株式会社

山口県宇部市大字沖宇部5253番地

(72) 発明者 近藤 剛

三重県松阪市大口町1510 セントラル硝子
株式会社硝子研究所内

(72) 発明者 山本 秀樹

三重県松阪市大口町1510 セントラル硝子
株式会社硝子研究所内

(74) 代理人 弁理士 西 義之

(54) 【発明の名称】 合わせガラス及びその製造方法

(57) 【要約】

【課題】 従来から使用されている合わせガラス用中間膜層に大きな影響を与えることなく、断熱性能や紫外線遮断性能や電波透過性能等の機能特性を付与した、特に自動車用窓ガラス等に好適な合わせガラスを得る。

【解決手段】 少なくとも2枚の透明ガラス板状体の間に、3層からなる合わせ中間膜を設けた合わせガラスにおいて、該3層中の第2の中間膜に機能性超微粒子を分散させたことを特徴とする合わせガラス及びその製造方法

【特許請求の範囲】

【請求項 1】少なくとも 2 枚の透明ガラス板状体の間に、3 層からなる合わせ中間膜を設けた合わせガラスにおいて、該 3 層中の第 2 層の中間膜に粒径が $0.2\mu\text{m}$ 以下の機能性超微粒子を分散せしめてなることを特徴とする合わせガラス。

【請求項 2】前記第 1 層及び第 3 層中間膜が、ポリビニルブチラール樹脂であることを特徴とする請求項 1 記載の合わせガラス。

【請求項 3】前記第 2 層中間膜が、ポリビニルブチラール樹脂または塩化ビニル樹脂であることを特徴とする請求項 1 または 2 記載の合わせガラス。

【請求項 4】前記機能性超微粒子の粒径が、 $0.15 \sim 0.01\mu\text{m}$ であることを特徴とする請求項 1 記載の合わせガラス。

【請求項 5】前記機能性超微粒子の混合割合が、 $10.0 \sim 0.01\text{wt}\%$ であることを特徴とする請求項 1 または 4 記載の合わせガラス。

【請求項 6】前記機能性超微粒子が、Sn、Ti、Si、Zn、Zr、Fe、Al、Cr、Co、In、Ni、Ag、Cu、Pt、Mn、Ta、W、V、Mo の金属、酸化物、窒化物、硫化物あるいは Sb や F のドーパ物の各単独物、もしくはこれらの中から少なくとも 2 種以上を選択してなる複合物であることを特徴とする請求項 1 記載の合わせガラス。

【請求項 7】前記合わせガラスが、自動車用窓ガラスであることを特徴とする請求項 1 記載の合わせガラス。

【請求項 8】少なくとも 2 枚の透明ガラス板状体の間に 3 層からなる中間膜層を設けた合せガラスを製造する方法において、該 3 層中の第 2 層の中間膜に $0.2\mu\text{m}$ 以下の機能性超微粒子を分散せしめ、少なくとも 2 枚のガラス板を合わせガラス化処理をすることを特徴とする合わせガラスの製造方法。

【請求項 9】前記第 2 層の中間膜は、粒径が $0.2\mu\text{m}$ 以下の機能性超微粒子を可塑性中に $80.0\text{wt}\%$ 以下分散せしめて機能性微粒子分散可塑性とし、次いで該機能性超微粒子分散可塑性を樹脂に対し $50\text{wt}\%$ 以下分散添加し、混合混練することで機能性超微粒子を均一に分散した原料樹脂からなる樹脂膜であることを特徴とする請求項 8 記載の合わせガラスの製造方法。

【請求項 10】前記第 2 層の中間膜が、ポリビニルブチラール樹脂を溶解する溶剤に粒径が $0.2\mu\text{m}$ 以下 $0.001\mu\text{m}$ 以上の機能性超微粒子を均一に分散した後、該溶剤を適宜可塑性ならびにその他の添加剤とともにポリビニルブチラール樹脂に均一に溶解させ混合混練したのち、該中間膜用原料樹脂からフィルム化し、 $50 \sim 110^\circ\text{C}$ で乾燥して得たポリビニルブチラール樹脂膜であることを特徴とする請求項 8 または 9 記載の合わせガラスの製造方法。

【請求項 11】前記第 2 層の中間膜は、ガラス転移点である $55 \sim 90^\circ\text{C}$ の温度以上に加熱して軟化したポリビニル

ブチラール樹脂に少なくとも前記粒径が $0.2\mu\text{m}$ 以下 $0.001\mu\text{m}$ 以上の機能性超微粒子を直接添加し混合混練して均一分散した中間膜用原料樹脂からなるポリビニルブチラール樹脂膜であることを特徴とする請求項 8 記載の合わせガラスの製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、接着性、透明性、耐久性に優れた性能を有する合わせガラスに関する。

【0002】

【従来の技術】近年、建築用ガラスにおけるクリアや着色、断熱や紫外線遮断および電波透過等の機能付与はもちろん、車輦用ガラスにおいても車内に通入する太陽輻射エネルギーを遮蔽し、車内の温度上昇、冷房負荷を低減させる目的から熱線遮蔽ガラス、さらに人的物的両面や環境に優しくするため紫外線遮蔽を付加したものが車輦用に採用されている。また最近には特に該車輦用ガラスにおいて、グリーン色調で充分な可視光透過率を有しながら高熱線紫外線遮蔽性能を持ちかつ各種電波の高透過性能が要求されるようになってきている。そのうち、微粒子あるいは超微粒子を合せガラスの中間層に分散するものとしては次のような出願が知られている。

【0003】例えば特開平 2-22152 号公報には、光吸収剤と微粒子状無機物質を可塑性ポリビニルブチラール樹脂に含有させた短波長光線遮断性合せガラス用中間膜が記載されており、特開平 4-160041 号公報には、超微粒子とガラス成分との混合層を透明板状部材間に形成してなる自動車用合わせガラスが記載されており、さらに特開平 4-261842 号公報には、エチレン・エチルアクリレート共重合樹脂に二酸化ケイ素微粒子を含有した中間膜を有する合わせガラス開示されている。さらに、当社出願の合わせガラス 2 件（特願平 07-007944 号、07-165489 号）には、合わせ中間膜に機能性微粒子を分散させた合わせガラスが開示されている。

【0004】しかし、前記の合わせガラスは機能性超微粒子を合わせ中間膜に混入させ、直接ガラスと該中間膜とを接着、積層処理し合わせたものであり、混入する粒子の種類、混入量、粒子径等により、ガラスと合わせ中間膜との接着強度が影響され、好ましいものではなかった。例えば、微粒子が酸化物系の場合には、ガラスとの接着強度が増加し、自動車用の場合には、合わせガラス破壊時における衝撃吸収力が低減し安全上の問題点があった。

【0005】

【発明が解決しようとする課題】本発明は、従来のこのような課題に鑑みてなしたものであり、従来から使用されている合せガラス用中間膜層に影響を与えることなく、中間膜層に機能性超微粒子を適宜分散し含有せしめることで、断熱性能や紫外線遮断性能や電波透過性能等の機能特性を付与し、しかもクリア乃至着色の色調の制

御および透視性の確保や反射性とぎらつき感の防止等をバランスよくもたらしめ、従来の合せガラスと変わらない品質を得るようにでき、特殊成分組成ガラスや特殊表面加工ガラスを必要とせず、かつ現在使用中の合せガラス製造ラインをそのままで合せガラス化処理作業で行うことができ、例えばガラスとガラス、ガラスとプラスチック、パイレイヤガラス等を安価にかつ容易にしかもガラスの大きさや形態に自由自在に対応し得て製造でき、建築用窓材はもちろん自動車用窓材、飛行機用窓材、ことに風防用ガラスにも充分適用でき、最近のニーズに最適なものとなる有用な機能性合せガラスを提供するものである。

【0006】

【課題を解決するための手段】本発明は、少なくとも2枚の透明ガラス板状体の間に、3層からなる合わせ中間膜を設けた合せガラスにおいて、該3層中の第2層の中間膜に粒径が $0.2\mu\text{m}$ 以下の機能性超微粒子を分散せしめてなるものとしたことを特徴とする合せガラスを提供する。

【0007】前記第1層及び第3層中間膜は、好ましくは、ポリビニルブチラル樹脂膜である。

【0008】前記第2層中間膜は、好ましくは、ポリビニルブチラル樹脂または塩化ビニル樹脂である。

【0009】前記機能性超微粒子の粒径は、より好ましくは、 $0.15\sim 0.001\mu\text{m}$ である。

【0010】前記機能性超微粒子の混合割合は、好ましくは、 $10.0\sim 0.01\text{wt}\%$ である。

【0011】前記機能性超微粒子は、Sn、Ti、Si、Zn、Zr、Fe、Al、Cr、Co、In、Ni、Ag、Cu、Pt、Mn、Ta、W、V、Moの金属、酸化物、窒化物、硫化物あるいはSbやFのドーパ物の各単独物、もしくはこれらの中から少なくとも2種以上を選択してなる複合物、またはさらに当該各単独物もしくは複合物に有機樹脂物を含む混合物または有機樹脂物を被覆した被膜物である。

【0012】前記合わせガラスは、自動車用窓ガラスとして好適である。

【0013】また、本発明は、少なくとも2枚の透明ガラス板状体の間に3層からなる中間膜層を設けた合せガラスを製造する方法において、該3層中の第2層の中間膜に機能性超微粒子を分散せしめ、少なくとも2枚のガラス板を合わせガラス化処理をすることを特徴とする合せガラスの製造方法を提供する。

【0014】また、本発明は、前記第2層の中間膜は、粒径が $0.2\mu\text{m}$ 以下の機能性超微粒子を可塑剤中に $80.0\text{wt}\%$ 以下分散せしめて機能性超微粒子分散可塑剤とし、次いで該機能性超微粒子分散可塑剤を樹脂に対し $50\text{wt}\%$ 以下分散添加し、適宜その他の添加剤を加え、混合混練することで機能性超微粒子を均一に分散した原料樹脂からなる樹脂膜であることを特徴とする合せガラスの製造方法を提供する。

【0015】さらに、本発明は、前記第2層の中間膜が、ポリビニルブチラル樹脂を溶解する溶剤に前記粒径が $0.2\mu\text{m}$ 以下 $0.001\mu\text{m}$ 以上の機能性超微粒子を均一に分散した後、当該溶剤を適宜可塑剤ならびにその他の添加剤とともにポリビニルブチラル系樹脂に均一溶解させ混合混練して膜用原料樹脂からフィルム化し、 $50\sim 110^\circ\text{C}$ で乾燥して得たポリビニルブチラル系樹脂膜であることを特徴とする合せガラスの製造方法を提供する。

【0016】さらにまた、本発明は、前記第2層の中間膜は、ガラス転移点である $55\sim 90^\circ\text{C}$ の温度以上に加熱して軟化したポリビニルブチラル樹脂に少なくとも前記粒径が $0.2\mu\text{m}$ 以下 $0.001\mu\text{m}$ 以上の機能性超微粒子を直接添加し混合混練して均一分散した膜用原料樹脂から得たポリビニルブチラル系樹脂膜であることを特徴とする合せガラスの製造方法を提供する。

【0017】

【発明の実施の形態】ここで、前記したように、第2の中間膜層の中に粒径が $0.2\mu\text{m}$ 以下の機能性超微粒子を分散せしめてなるものとしたのは、可視光域の散乱反射を抑制しながら、例えば日射透過率が 65% 以下等熱線遮蔽性能等超微粒子の機能特性を充分発揮しつつ、超低ヘーズ値、電波透過性能、透明性を確保するためと、超微粒子を含有せしめても従来の合せガラス用中間膜として例えば接着性、透明性、耐久性等の物性を維持し、通常の合せガラス製造ラインで通常作業で合せガラス化処理ができるようにするためである。好ましくは粒径が $0.15\mu\text{m}$ 以下程度であり、より好ましくは約 $0.10\sim 0.001\mu\text{m}$ 程度である。なお粒径分布の範囲については、例えば約 $0.03\sim 0.01\mu\text{m}$ 程度と均一化されていることがよい。

【0018】また、第2の中間膜層への機能性超微粒子の混合割合が $10.0\text{wt}\%$ 以下であるとしたのは、可視光域の散乱反射を抑制しながら、例えば日射透過率が 65% 以下などの熱線遮蔽性能等超微粒子の機能特性を充分発揮する量を確保し、さらに低ヘーズ値、電波透過性能、透明性であるようにし、しかも超微粒子を含有せしめても従来の合せガラス用中間膜として例えば接着性、透明性、耐久性等の物性を維持し、通常の合せガラス製造ラインによる通常作業で合せガラス化処理ができるようにするために、前記粒径とも深い関係にあり、 $10.0\text{wt}\%$ を超えるとなると次第に上記要件を特に自動車用窓材はもちろん建築用窓材としても実現し難くなるためである。ことに例えば建築用合せガラス向けとして可視光透過率 T_v が 35% 以上の場合は無機顔料系超微粒子の混合割合が約 $10\sim 0.1\text{wt}\%$ 程度必要であり、建築用としては約 $9\sim 0.01\text{wt}\%$ 程度、より好ましくは $8\sim 0.05\text{wt}\%$ 程度であり、自動車用としては好ましい混合割合としては約 $2.0\sim 0.01\text{wt}\%$ 程度、より好ましくは $1.5\sim 0.05\text{wt}\%$ 程度、さらに好ましくは $1.0\sim 0.1\text{wt}\%$ 程度である。いずれにしても合せガラスとしての性能保持とめざす機能性

能との兼ね合いでその混合割合（含有量）は決定されるものである。

【0019】さらに、中間膜が、ポリビニルブチラール系樹脂膜(PVB系)したのは、これらが合せガラス用中間膜として汎用性のものであるから好ましく、合せガラスとしての品質をニーズに整合し得るような中間膜層となるものであれば特に限定するものではない。具体的には可塑性PVB〔積水化学工業社製、三菱モンサント社製等〕、紫外線吸収剤、抗酸化剤、帯電防止剤、熱安定剤、滑剤、充填剤、着色、接着調整剤等を適宜添加配合

【0020】また、中間膜としてエチレン-酢酸ビニル共重合体樹脂を用いることもでき、その場合には、第2の中間膜も同じ樹脂を用いることが好ましく、特に建築用合わせガラスに適する。

【0021】なお、中間膜として、本超微粒子入り中間膜と従来の中間膜とを、例えば両者を重ね合わせる。あるいは本超微粒子入り中間膜を従来の中間膜でサンドイッチする等の構成とするものとしてもよい。

【0022】またさらに、機能性超微粒子が、Sn、Ti、Si、Zn、Zr、Fe、Al、Cr、Co、Ce、In、Ni、Ag、Cu、Pt、Mn、Ta、W、V、Moの金属、酸化物、窒化物、硫化物あるいはSbやFのドーパ物の各単独物、もしくはこれらの中から少なくとも2種以上を選択してなる複合物、またはさらに当該単独物もしくは複合物に有機樹脂を含む混合物または有機樹脂物を被覆した被膜物であるものとしたのは、各単独もしくは複合物、混合物、被膜物として断熱性能、紫外線遮蔽性能、着色性能、遮光性等を適宜発現し、建築用や自動車用に求められる種々の機能性および性能を合せガラスとして発現せしめるためである。

【0023】また機能性超微粒子としては、例えばSn、Ti、Si、Zn、Zr、Fe、Al、Cr、Co、Ce、In、Ni、Ag、Cu、Pt、Mn、Ta、W、V等のほかMoなどの各種金属。例えばSnO₂、TiO₂、SiO₂、ZrO₂、ZnO、Fe₂O₃、Al₂O₃、FeO、Cr₂O₃、Co₂O₃、CeO₂、In₂O₃、NiO、MnO、CuO等の各種酸化物。例えばTiN、AlN等の窒化物、あるいは窒素酸化物。例えばZnS等の硫化物。例えば9wt% Sb₂O₃-SnO₂(ATO)〔住友大阪セメント社製〕、F-SnO₂等のドーパ物。さらに例えばSnO₂-10wt% Sb₂O₃、In₂O₃-5wt% SnO₂(ITO)〔三菱マテリアル社製〕等の複合物である。なお、ATOやITOは自動車用としてその要件を備え特に好ましいものである。

【0024】さらに例えばCo₂O₃-Al₂O₃(TM3410、0.01~0.02μm)、TiO₂-NiO-Co₂O₃-ZnO(TM3320、0.01~0.02μm)、Fe₂O₃-ZnO-Cr₂O₃(TM3210、0.01~0.02μm)〔それぞれ大日精化工業社製〕等の無機顔料微粒子が挙げられ、また例えば具体的にはTiO₂超微粒子としてはIT-S-UD

〔0.02μm、出光石油化学社製〕、UF01〔0.018μm、タイオキサイド・ケミカルズ社製〕等、Fe₂O₃微粒子としてはナノタイト〔微粒子球形ヘマタイト、0.06μm、昭和電工社製〕等が挙げられ、具体的に挙げていない微粒子でも適宜必要に応じて求められる機能特性を合せガラスの品質を維持しつつ発揮することができるものであれば特に限定することなく使用できることは言うまでもない。

【0025】またさらに、有機系紫外線吸収剤あるいは有機系熱線吸収剤については、有機系紫外線吸収剤としては例えば2-(2'-ヒドロキシ-5'-メチルフェニル)ベンゾトリアゾール、2-(2'-ヒドロキシ-3',5'-ジ・tert-ブチルフェニル)ベンゾトリアゾール、2-(2'-ヒドロキシ-3'-tert-ブチル-5'-メチルフェニル)-5-クロロベンゾトリアゾール、2-(2'-ヒドロキシ-3',5'-ジ・tert-ブチルフェニル)-5-クロロベンゾトリアゾール、2-(2'-ヒドロキシ-3',5'-ジ・tert-アミルフェニル)ベンゾトリアゾール等のベンゾトリアゾール系誘導体、また例えば2,4-ジヒドロキシベンゾフェノン、2-ヒドロキシ-4-メトキシベンゾフェノン、2-ヒドロキシ-4-オクトキシベンゾフェノン、2-ヒドロキシ-4-ドデシルオキシベンゾフェノン、2,2'-ジヒドロキシ-4-メトキシベンゾフェノン、2,2'-ジヒドロキシ-4,4'-ジメトキシベンゾフェノン、2-ヒドロキシ-4-メトキシ-5-スルホベンゾフェノン等のベンゾフェノン系誘導体、また2-エチルヘキシル-2-シアノ-3,3'-ジフェニルアクリレート、エチル-2-シアノ-3,3'-ジフェニルアクリレート等のシアノアクリレート系誘導体などが挙げられる。具体的には例えばTINUVIN327〔チバガイギー社製〕等である。

【0026】さらに有機系熱線吸収剤としては例えばNIR-AM1〔帝国化学産業社製〕、ことに近赤外線吸収剤としてはSIR-114、SIR-128、SIR-130、SIR-132、SIR-169、SIR-103、PA-1001、PA-1005〔三井東圧化学社製〕等が挙げられる。特に建築用や自動車用に求められる合せガラスの品質を維持しつつ発揮するものであれば、限定することなく使用できることは言うまでもない。

【0027】またさらに、前記した構成でなる合せガラスは種々の建築用窓材等として使用できることはもちろん、特に自動車用窓材として例えばフロントガラス、リアガラスことにシェードバンド付きリアガラス、サイドガラスあるいはサンルーフガラスあるいは他の種々のガラス等に使用できるものである。

【0028】また、一般にガラスアンテナ付きガラスのシート抵抗値としては、例えば20kΩ/口以上の抵抗値であって、特にアンテナと接触する際には、10MΩ/口以上の高抵抗値であることが好ましく、10MΩ/口未満のシート抵抗値では、積層体にする以前のガラス板の電波透過性に比し充分安定確実に1dB（絶対値として）以内の変動差内に収めることができないものであり、より

充分安定確実に1dB以内の変動差内、例えば0.8dB以内の変動差内とするためには15MΩ/□以上、さらに電波透過性能および光学特性ならびに物理的化学的特性を充分満足する好ましい積層体のシート抵抗値としては20MΩ/□以上10GΩ/□以下程度の範囲であり、より好ましいシート抵抗値としては22MΩ/□以上10GΩ/□以下程度の範囲である。

【0029】該ガラス板状体とはほぼ同等の電波透過性能を有する前記積層体と特に光学特性上で巧みに相互に絡ませ相乗効果をもたらしめるようにすることで、電波透

過性能および熱線遮蔽性能を高めたことはもちろん、格段に優れた光学的機能を備える卓越した特に自動車用窓ガラスとして最適なものとしたものである。

【0030】すなわち、自動車用窓ガラスとして、電波透過性能を前記ガラス板状体に限り無く近づけほぼ同等としかつ熱線遮蔽性能を日射透過率が65%以下と格段に高め居住性をさらに向上したなかで、運転者や搭乗者等が安全上等で必要である可視光透過率を65%以上とした透視性、例えば可視光透過率が70%以上等を確保し法規上もクリアできるようにでき、しかも運転者や搭乗者等における透視性低下、誤認あるいは目の疲労等の防止に必要である可視光反射率を従来の値よりさらに低減せしめることができ、最適な電波透過型熱線紫外線遮蔽合

セガラスとなる。自動車用として好ましくは可視光透過率が68~70%以上、可視光反射率が14%以下、しかも日射透過率が60%以下、刺激純度が15~10%以下であり、建築用として好ましくは可視光透過率が30%以上、可視光反射率が20%以下、しかも日射透過率が65%以下、刺激純度が20%以下である。

【0031】さらにまた、前記電波透過型熱線紫外線遮蔽の合セガラスは、例えばガラス板状体の周辺部の黒枠内で周縁端からある幅で全周部分または給電点部よりやや大きめの部分を除いて、あるいは該給電点部と同様にししかもモール（枠体）を一体成型または後付けする部分を除き、さらには該アンテナ導体部分の全部または一部を除いて超微粒子を含む機能性中間膜を採用する等、その構成は適宜自在になし得ることは言うまでもない。

【0032】さらにまた、中間膜が熱線遮蔽性能を有しかつシート抵抗値を半導体膜乃至絶縁膜と高い値であることにより、AM電波、FM電波等の放送における受信障害あるいはTV映像でのゴースト現象等の電波障害などをより確実に発現しないようにすることができ、十分な電波透過性能を有するガラスを得て、環境に優しいものとするることができるものである。また例えば、ガラスアンテナ素子に前記高抵抗の熱線遮蔽性能を有する膜を直接積層した場合においても、電波受信性能の低下には影響を及ぼすことがないようにしたと言えるものとなるものである。

【0033】また、前記のようにガラス板状体としては無機質ガラス、有機ガラスあるいはこれらの複合ガラ

ス、特に所謂フロート法で製造された無機質で透明なクリア乃至着色ガラス、強化ガラスやそれに類するガラス、プライマーや各種機能性膜等被覆膜付きガラスであって、好ましくは例えばグリーン系ガラスやブロンズ系ガラスであり、さらに例えばグレー系ガラスやブルー系ガラス等にも採用可能である。また合セガラスのほか複層ガラス、バイレヤーガラス等、さらに平板あるいは曲げ板等各種板ガラス製品として使用できることは言うまでもない。また板厚としては例えば約1.0mm程度以上約12mm程度以下であり、建築用としては約2.0mm程度以上約10mm程度以下が好ましく、自動車用としては約1.5mm程度以上約3.0mm程度以下が好ましく、より好ましくは約2.0mm程度以上約2.5mm程度以下のガラスである。

【0034】さらに、ポリビニルブチラール樹脂膜またはエチレン-酢酸ビニル共重合体樹脂膜が、粒径が0.2μm以下の機能性超微粒子を可塑剤中に80.0wt%以下分散せしめて機能性超微粒子分散可塑剤とし、次いで該機能性超微粒子分散可塑剤をポリビニルブチラール系またはエチレン-酢酸ビニル共重合体樹脂溶液中に、ポリビニルブチラール系またはエチレン-酢酸ビニル共重合体樹脂に対し機能性超微粒子分散可塑剤を50wt%以下少なくとも分散添加し、適宜その他の添加剤を加え、混合混練して膜用原料樹脂から得たこととしたのは、可塑剤溶液中に前記機能性超微粒子を分散せしめる方が分散し易く、粒径が0.2μm以下の機能性超微粒子の分散を充分均一化することができ、透明性が得られるためであり、その混合量が80.0wt%を超えると次第に分散が難しくな

って均一化が確実でなくなり易くなるためであり、好ましくは20.0wt%程度以下、より好ましくは10.0wt%程度以下、さらに好ましくは5.0wt%以下0.5wt%以上程度であって、少なすぎても前記効果がなくなる。

【0035】また、ポリビニルブチラールまたはエチレン-酢酸ビニル共重合体樹脂に対し機能性超微粒子分散可塑剤の分散添加が50wt%を超えると、ポリビニルブチラールまたはエチレン-酢酸ビニル共重合体樹脂中での分散のみでなく、合セガラスの中間膜としての性能に支障をきたすようになり易いからであり、好ましくは45wt%程度以下、より好ましくは40wt%程度以下10wt%程度以上である。また、混合混練には通常のみキサー、パンバリーミキサーやブラベンダーミキサー、ニーダー等を用いる。

【0036】さらにまた、可塑剤としては、例えばジオクチルフタレート(DOP)、ジイソデシルフタレート(DIDP)、ジトリデシルフタレート(DTDP)、ブチルベンジルフタレート(BBP)などのフタル酸エステル、またトリクレシルホスフェート(TCP)、トリオクチルホスフェート(TOP)などのリン酸エステル、またトリブチルシトレート、メチルアセチルリシノレート(MAR)などの脂肪酸エステル、またトリエチレングリコール・ジ-2-エチルブチレート(3GH)、テトラエチレングリコール・ジヘキサ

ノールなどのポリエーテルエステルなど、またさらにこれらの混合物が挙げられる。

【0037】さらに、前記PVB系樹脂を溶解する溶剤としては、例えばエチルアルコール、n-プロピルアルコール、イソプロピルアルコール、n-ブチルアルコール、メチレンクロライド等が挙げられる。さらにまた、前記EVA系樹脂を溶解する溶剤としては、例えばトルエン、キシレン、メチレンクロライド等が挙げられる。

【0038】さらに、前記中間膜用原料樹脂のフィルム化としては、常法の型押し法またはカレンダーロール法等である。中間膜の膜厚としては約0.2~1.2mm程度、好ましくは約0.3~0.9mm程度である。

【0039】さらに、前記合せガラス化処理としては、オートクレープ法、減圧下で常温から120℃まで昇温する中で80~120℃の温度範囲で20~30分間の加熱等であり、膜表面に均一な凹凸のしぼを設ける。なお、場合によって種々の簡易な合せガラス化処理を適宜適用できることは言うまでもない。

【0040】

【作用】前述したとおり、本発明の合せガラスは、着色、熱線や紫外線遮断膜、電波透過等各種の機能性能を有する超微粒子を第2層の中間膜中に適宜分散含有せしめ、合せ処理することでなる合せガラスとその製造方法としたことにより、従来から使用されている合せガラス用中間膜層に影響を与えることなく、断熱性能や紫外線遮断性能や電波透過性能等の機能特性を付与し、しかもクリア乃至着色の色調の制御およびヘーズ値が極めて低く優れた透視性の確保ならびに反射性とざらつき感の防止等をバランスよくもたらしめ、例えば自動車用安全ガラスに係わるJIS R 3212の各試験等をクリアする等、従来の合せガラスと変わらない品質を得ることができ、特殊成分組成ガラスや特殊表面加工ガラスを必要とせず、かつ現在使用中の合せガラス製造ラインをそのままで合せガラス化処理と作業で行うことができ、安価にかつ容易にしかもガラスの大きさや形態に自由自在に対応し得て合せガラスを得ることができるものである。また塩化ビニル系樹脂膜を接着積層した複合膜を用いた合せガラスは前述した特性に加え耐貫通性、防音性等にも優れるものとなり、フロントウィンドシールドガラスとして有用な自動車用窓ガラスとなる等、透視性、耐候性ならびに耐衝撃性等も優れ、車内の乗員の安全性ならびに居住性等に寄与することができる自動車用窓ガラスを提供するものである。

【0041】ひいては、冷暖房効果を高め居住性を向上せしめるような優れた日射透過率、環境や人に優くなる紫外線遮断等を有するとともに、比較的高いものから低いものまで幅広い可視光線透過率を有するものとすることができ、AM電波、FM電波TV電波帯等の放送における受信障害などの低減をすることができ、通常のフロートガラス並の電波透過性能であることから、車輛用のテレ

ビ、ラジオ、携帯電話等のためのガラスアンテナの受信性能を低下させることなく、あるいはゴースト現象等の電波障害を低減することができ、本来のガラスアンテナ性能を発揮させ、車輛内外での快適な環境を確保することができることとなり、電波透過性能を必要とする無色から有色と各種色調、或いはガラスとガラス、ガラスと合成樹脂板、バイレヤー等の合せガラスとして使用可能な電波透過型熱線紫外線遮蔽ガラス等となり、建築用窓材としてはもちろん、特に自動車用窓材、例えばフロントウィンドー、リヤウィンドーあるいはサイドウィンドーまたはサンルーフ、シェードバンド等に、ことに風防用ガラスにも充分適用でき、また飛行機用窓材等幅広く適用でき、最近のニーズに最適なものとなる有用な機能性を有する合せガラス及びその製造方法を提供するものである。

【0042】

【実施例】以下、実施例により本発明を具体的に説明する。ただし本発明に係る実施例に限定されるものではない。

【0043】実施例1

20wt%ATO(導電性アンチモン含有錫酸化物)超微粒子(粒径0.02μm以下)分散含有DOP(ジオクチルフタレート)10gと通常のDOP100gをPVC(ポリ塩化ビニル)樹脂450gに添加し、他の紫外線吸収剤等とともに3本ロールのミキサーにより約70℃で約15分間程度練り込み混合した。得られた製膜用原料樹脂を型押し機にて190℃前後で厚み約0.8mm程度にフィルム化しロールに巻き取った。これをフィルム(A)とする。

【0044】次にポリビニルブチラル樹脂から得られた2枚の膜(B)とフィルム(A)とを、積層構成がポリビニルブチラル樹脂層(B)/ポリ塩化ビニル樹脂層(A)/ポリビニルブチラル樹脂層(B)になるように重ね合わせて、3層の積層中間膜を得た。この中間膜をそれぞれ1辺30cmの正方形の厚み2.3mmの2枚のフロートガラスで両側からサンドイッチし、この未圧着サンドイッチ体をゴムバックに入れ、20torrの真空度で20分間脱気した後、脱気状態のまま90℃のオーブンに移し、この温度を30分間保持した。こうして真空プレスにより仮圧着したサンドイッチ体を、ついでオートクレープ中に圧力12Kg/cm²、温度135℃で熱圧着処理し、透明な合わせガラスを作製した。

【0045】次いで該積層体をゴム製の真空袋に入れ、袋内を脱気減圧し、約80~110℃程度で約20~30分程度保持した後一旦常温までにし、袋から取り出した積層体をオートクレープ装置に入れ、圧力約10~14kg/cm²、温度約110~140℃程度で約20~40分間程度の加圧加熱して合せガラス化処理をした。

【0046】得られた合せガラスについて下記の測定および評価を行った。

【光学特性】：分光光度計(340型自記、日立製作所

製)で波長340~1800nmの間の透過率を測定し、JIS Z 8722及びJIS R 3106又はJIS Z 8701によって可視光透過率 T_v (380~780nm)、日射透過率 T_s (340~1800nm)、刺激純度(%)、色調等を求めた。

〔くもり度〕：ヘーズ値 H をJIS K6714に準拠して行い求めた。建築用としては3%以下、自動車用としては1%以下を合格とした。

〔電波透過性〕：KEC法測定(電界シールド効果測定器)によって、電波10~1000MHzの範囲の反射損失値(dB)を通常の板厚3mmのクリアガラス(FL3t)単板品と対比。その差の絶対値(Δ dB)が2dB以内を合格とした。

〔接着性〕：-18 \pm 0.6℃の温度で16 \pm 4時間放置し調整後、ハンマー打でのガラスの剥離での中間膜露出程度。少ないものを合格とした。

〔耐熱性〕：100℃の煮沸水中にて2時間程度煮沸した後、周辺10mmを除き、残りの部分での遮の発生、くもり、ガラスのひび割れ等の異常がないものを合格とした。

〔耐湿性〕：50 \pm 2℃、相対湿度95 \pm 4%の調整内に2週間静置した後、遮の発生、くもり、ガラスのひび割れ等の異常がないものを合格とした。

〔電気的特性〕：三菱油化製表面高抵抗計(HIRESTA HT-210)によって測定。10M Ω /口(シート抵抗値)以上合格。

【0047】結果、可視光透過率 T_v が約77.7%程度、日射透過率 T_s が約55.0%程度、刺激純度 P_e が0.7%程度で淡いグレー系のニュートラル色調、反射によるギラツキもなく、ヘーズ値 H が約0.3%程度となり、充分優れた熱線遮蔽性等の光学特性、格段に高い表面抵抗率で通常単板ガラス並み、例えば80MHz(FMラジオ波帯)、約520~1630kHz(AMラジオ波帯)等特に通常単板ガラスと同等の電波透過性を示し、かつ充分安定な優れた接着性と耐熱性ならびに耐湿性を示しいずれも合格であり、通常の合せガラスと変わらない合せガラスを得ることができ、優れた居住性をもちかつ運転者や搭乗者あるいは環境に優しく安全性が高くしかもAM帯をはじめ各種電波を快適に受信ができ、建築用窓ガラスはもちろん自動車用窓ガラスに対しても充分採用でき、期待に充分答えることができるものであった。

【0048】なお、他に耐候性(例、サンシャインウエザーメーターで約1000時間：可視光透過率がほぼ変化がないこと)等の種々の特性をも評価したところ、いずれも合格するものであった。

【0049】さらに、同様の構成の自動車用窓ガラスにおいて、前記中間膜を10℃~50℃の温度範囲に保持するよう制御したところ、上述したと同様の結果を得、車室内の静粛性に充分寄与するものであった。

【0050】なお、得られた試料を、音響放射パワーの測定システムによって音響放射パワーを測定し、残響室

法によって音響透過損失を測定し、さらにJIS 3211、JIS 3212ならびにJIS R3205等の規定に準じて評価を行ったところ、所期の自動車用窓ガラスとしての性能を充分備え優れたものであった。

【0051】実施例2

20wt%ATO(導電性アンチモン含有錫酸化物)超微粒子(粒径0.02 μ m以下)分散含有3GH(トリエチレングリコール-ジ-2-エチルブチレート)10gと通常の3GH130gをPVB(ポリビニルブチラル)樹脂485gに添加し、さらに接着調整剤としてトスパール120(東芝シリコン)を5g添加し、他の紫外線吸収剤等とともに3本ロールのミキサーにより約70℃で約15分間程度練り込み混合した。得られた製膜用原料樹脂を型押出機にて190℃前後で厚み約0.8mm程度にフィルム化しロールに巻き取り、実施例1と同様にしてポリビニルブチラル樹脂フィルムでサンドイッチして3層積層体を得た。

【0052】次に大きさ約300mm \times 300mm、厚さ約2.0mmのクリアガラス基板(FL2)を用いて実施例1と同様にして合わせた。次いで実施例1と同様にして合せガラス化処理をした。

【0053】得られた合せガラスは、 T_v が80.2%、 T_s が58.5%、 H が0.4%等実施例1と同様に優れた光学特性ならびに電波透過性、品質等の各物性をバランスよく示す所期のものであった。

【0054】実施例3

20wt%ITO(導電性錫含有インジウム酸化物)超微粒子(粒径0.1 μ m以下)分散含有BBP(ブチルベンジルフタレート)10gと通常のBBP70gをPVC樹脂300gに添加し、実施例1と同様にして合わせガラス化処理をした。

【0055】次に大きさ約300mm \times 300mm、厚さ約2.0mmのクリアガラス基板(FL2)を用いて実施例1と同様にして積層体とした。次いで実施例1と同様にして合せガラス化処理をした。

【0056】得られた合せガラスは、 T_v が71.3%、 T_s が46.1%、 H が0.4%等実施例1と同様に優れた光学特性ならびに電波透過性、品質等の各物性をバランスよく示す所期のものであった。またパンメル値は7~8程度であり、建築用合せガラスに適するものであった。

【0057】なお、パンメル値については、実施例1と2においても実施例3のようにして適宜建築用あるいは自動車用として調整して用いることができることは言うまでもない。

【0058】

【発明の効果】以上前述したように、本発明は機能性超微粒子を中間膜層に分散含有する合せガラス及びその製造方法としたことにより、従来から使用されている合せガラス用中間膜層に大きな影響を与えることなく、断熱性能や紫外線遮断性能や電波透過性能等の機能特性を付与し、しかもクリア乃至着色の色調の制御およびヘーズ値が極めて低く優れた透視性の確保ならびに反射性とき

らつき感の防止等をバランスよくもたらしめ、従来の合せガラスと変わらない品質を得るようにでき、現在使用中の合せガラス製造ラインをそのまま合せガラス化処理と作業で行うことができ、安価にかつ容易にしかもガラスの大きさや形態に自由自在に対応し得て実施でき、ひいては冷暖房効果を高め居住性を向上せしめ、環境や人に優しく、幅広い透視性を得ることができ、AM電波、FM電波TV電波帯等を通常のフロートガラス並の電波透過性能として車輛用のテレビ、ラジオ、携帯電話等のためのガラスアンテナ性能を確保でき、本来のガラスアンテナ性能を発揮させ、建屋や車輛内外での快適な環境を確保することができることとなり、無色から有色と各種色調の合せガラスとして使用可能な電波透過型熱線紫外線

遮蔽ガラス等となり、各種建築用窓材としてはもちろん、特に各種自動車用窓材、ことに風防用ガラス、また飛行機用窓材、その他産業用ガラス等幅広く適用でき、最近のニーズに最適なものとなる有用な機能性を有する合せガラス及びその製造方法を提供することができる。また前述したように、本発明の自動車用窓ガラスによれば、損失係数を最大値付近で確保し、ガラス全体を高制振的性能とすることができ、音響・振動ならびに遮音等の各特性に優れ、車室内のこもり音を含む車内騒音を低減して静粛性を得、しかも透視性、耐候性ならびに耐衝撃性あるいは耐貫通性に優れるものとなる等、より高安全性ならびに高居住性を有する自動車用窓ガラスを提供するものである。

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☒ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.